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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Washington D.C. 20231
United States of America

in its capacity as elected Office

Date of mailing: 26 May 1995 (26.05.95)	
International application No.: PCT/AU94/00351	Applicant's or agent's file reference:
International filing date: 27 June 1994 (27.06.94)	Priority date: 15 November 1993 (15.11.93)
Applicant: ECCLES, Anthony, Philip	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International preliminary Examining Authority on:

03 April 1995 (03.04.95)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was [ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 730.91.11

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NOTIFICATION CONCERNING DOCUMENT TRANSMITTED

To:

United States Patent and Trademark Office
(Box PCT)
Washington D.C. 20231
United States of America

in its capacity as elected Office

Date of mailing (day/month/year) 23 October 1995 (23.10.95)	
International application No. PCT/AU94/00351	**International filing date** (day/month/year) 27 June 1994 (27.06.94)
Applicant APECS INVESTMENT CASTINGS PTY. LTD. et al	

The International Bureau transmits herewith the following documents and number thereof:

________ copy of the international preliminary examination report and annexes (Article 36(3)(a))

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer C. Carrié Telephone No.: (41-22) 730.91.11

Form PCT/IB/310 (July 1992)

000884764

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REC'D 17 OCT 1995
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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference CTG:mlh/1623	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International application No. **PCT/AU 94/00351**	International filing date 27 June 1994	Priority Date 15 November 1993

International Patent Classification (IPC) or national classification and IPC

Int. Cl.⁶ C22C 5/08, 5/06, 9/00, 9/04, 9/10, 30/06, 30/02, 1/03

Applicant
(1) APECS INVESTMENT CASTINGS PTY LTD
(2) ECCLES, Anthony Philip

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of **5** sheets, including this cover sheet.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of **14** sheet(s).

3. This report contains indications relating to the following items:

I	[X]	Basis of the report
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[X]	Lack of unity of invention
V	[X]	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[X]	Certain observations on the international application

Date of submission of the demand 3 April 1995	Date of completion of the report 5 October 1995
Name and mailing address of the IPEA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (06) 285 3929	Authorized Officer **R. HOWE** Telephone No. (06) 283 2159

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/AU 94/00351

I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

☐ the international application as originally filed.

☒ the description, pages , ~~as originally filed,~~
pages , filed with the demand,
pages , filed with the letter of ,
pages 1-9, filed with the letter of 21 July 1995.

☒ the claims, Nos. , as originally filed,
Nos. , as amended under Article 19,
Nos. , filed with the demand,
Nos. 1-20, filed with the letter of 21 July 1995,
Nos. , filed with the letter of .

☐ the drawings, sheets/fig , as originally filed,
sheets/fig , filed with the demand,
sheets/fig , filed with the letter of ,
sheets/fig , filed with the letter of .

2. The amendments have resulted in the cancellation of:

☐ the description, pages

☐ the claims, Nos.

☐ the drawings, sheets/fig

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

☐ restricted the claims.

☐ paid additional fees.

☐ paid additional fees under protest.

☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

☒ complied with.

☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☒ all parts.

☐ the parts relating to claims Nos.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims **1-20**	**YES**
	Claims	**NO**
Inventive step (IS)	Claims **1-20**	**YES**
	Claims	**NO**
Industrial applicability (IA)	Claims **1-20**	**YES**
	Claims	**NO**

2. Citations and explanations

None of the citations listed in the International Search Report disclose the work hardenable, firescale resistant silver alloy compositions which the applicant has selected for these properties.

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 1 is indefinite and speculative as it is not explicitly stated that silver (and inevitable impurities) make up the balance of the alloy composition.

See, for example, Mond Nickel (1948) 65 RPC 123.

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SILVER ALLOY COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to silver alloy compositions.

This invention has particular reference to sterling silver alloy compositions of silver content of at least 92.5% for jewellery, flatware, coinage and other applications where a work hardening alloy is required and for illustrative purposes reference will be made to this application. However, it is to be understood that this invention could be used to produce other types of silver alloys suitable for use as for example, electrical contacts or the like.

BACKGROUND OF THE INVENTION

In general, silver as a material for the production of silver jewellery, certain coinage and the like is specified to be sterling silver comprising at least 925 parts per thousand by weight fine silver and is specified as ".925 silver". .925 silver accordingly typically comprises an alloy 92.5% by weight silver, generally alloyed with copper for hardness traces of other metals as additives or impurities.

Conventional silver alloys of the .925 type have several disadvantages in a manufacturing jewellery and other materials engineering contexts. Principal limitations include a characteristic firescale formation tendency attributable to oxidation of copper and other metals at the surface of cast or hot worked pieces. Additionally, traditional alloys have exhibited undesirable porosity in the recast metal and less than desirable grain size properties.

Several formulations have been proposed to overcome one or the other of the aforementioned disadvantages. United States Patent Nos. 5039479 and 4973446 disclose alloys of silver and master alloys for the production of such silver alloys having superior qualities over conventional alloys, and including, in addition to silver, controlled amounts of copper and zinc, together with tin, indium, boron and silicon.

The compositions exhibit reduced porosity, grain size and

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fire scale production, and have acquired wide utilization in silver jewellery production. It is presumed but not established that the addition of zinc to such compositions provides at least a degree of antioxidant properties to the compositions when hot worked and improves colour, thus limiting the formation of principally copper oxide based fire scale, and reducing silver and copper oxide formation resulting in formation of pores in the cast or recast alloys. Silicon appears also to function as an antioxidant, thereby reducing firescale formation.

A disadvantage of the hereinbefore described firescale resisting alloys is that the alloys exhibit poor work hardening qualities thus not achieving the mechanical strength of traditional worked .925 silver goods.

DISCLOSURE OF THE INVENTION

The present invention aims to provide silver alloy compositions which substantially alleviate at least one of the foregoing disadvantages. A further object of the present invention is to provide silver alloys having the desirable properties of reduced fire scale, reduced porosity and oxide formation and reduced grain size relative to traditional sterling silver alloys whilst providing improved work hardening performance over the current firescale resistant alloys. Other objects and advantages of this invention will hereinafter become apparent.

With the foregoing and other objects in view, this invention in one aspect resides broadly in firescale resistant, work hardenable jewellery silver alloy compositions comprising:-

0.5 - 6% by weight copper;

0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and

0.01 - 2.5% by weight germanium.

The silver content of the alloy may be selected to be in the amounts commonly specified for grading silver. For example, the alloy may comprise from about 89 to 95% by

weight silver. Preferably, the alloy contains a proportion of silver required for the graded application to which the alloy is to be put, such as .925 silver, that is at least 92.5% by weight, for sterling silver applications and at least 90% by weight for coinage.

The copper content of the alloy may be selected according to the hardness required of the cast alloy. For example, for manufacturing jewellers .925 alloy, the copper content may advantageously be in the range of from about 2.0 to 3.0% by weight.

The zinc content of the alloy has a bearing on the colour of the alloy as well as functioning as a reducing agent for silver and copper oxides. Preferably, the amount of zinc used is selected to be between about 2.0 and 4.0% by weight. The silicon content of the alloy is preferably adjusted relative to the proportion of zinc used to provide the desired firescale resistance whilst maintaining a suitable colour commensurate with the zinc content of the alloy, and may for example advantageously fall within the range of about 0.15 to 0.2% by weight.

The germanium content of the alloy has surprisingly resulted in alloys having work hardening characteristics of a kind with those exhibited by conventional .925 silver alloys, together with the firescale resistance of the hereinbefore described firescale resistant alloys. In general, it has been determined that amounts of germanium in the alloy of from about 0.04 to 2.0% by weight provide modified work hardening properties relative to alloys of the firescale resistant kind not including germanium. However, it is noted that the hardening performance is not linear with increasing germanium nor is the hardening linear with degree of work.

Preferably, the alloy also includes rheology modifying and other additives to aid in improving the castability and/or wetting performance of the molten alloy. For example, about 0.0 to 3.5% by weight of a modifying additive selected from one or a mixture of indium and boron may be advantageously

added to the alloy to provide grain refinement and/or reduce surface tension, thereby providing greater wettability of the molten alloy. Where used, preferably the amount of boron utilized in the composition is from about 0 to 2% by weight boron and/or about 0 to 1.5% by weight indium. Other alloying elements may be added such as gold, tin or platinum. Where tin is included in the composition, this may be advantageously used up to about 6% by weight, and is preferably utilized in an amount of from about 0.25 to 6%.

Accordingly, in a further aspect, this invention resides in silver alloy compositions including:-

81 - 99.409% by weight silver;
0.5 - 6% by weight copper;
0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
0.001 - 2% by weight boron;
0.01 - 1.5% by weight indium, and
0.01 - 2.5% by weight germanium.

In a further aspect, this invention resides in silver alloy compositions including:-

75 - 99.159% by weight silver;
0.5 - 6% by weight copper;
0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
0.001 - 2% by weight boron;
0.01 - 1.5% by weight indium;
0.01 - 2.5% by weight germanium, and
0.25 - 6.0% by weight tin.

Of course, it is of advantage to the manufacturing metallurgist to be able to alloy fine silver without having to individually measure components. Accordingly, it is preferred that the compositions of the present invention be formed by the addition of a master alloy to fine silver. This also has the advantage that the master alloys are easier to transport than the made up alloys. Additionally, oxidizable components of the alloy are more stable to

atmospheric oxidation when alloyed. Accordingly, in a further aspect this invention resides broadly in a method of producing firescale resistant, work hardenable silver alloy compositions and including the alloying of silver metal with a master alloy comprising, by weight:

52.5 - 99.85% by weight copper;

0.1 - 35% by weight of zinc or silicon or mixtures thereof, and

0.05 - 12.5% by weight germanium.

For production of the preferred modified alloys, there may be provided master alloys including additional alloying elements such as up to about 10% by weight boron, up to about 15% by weight indium and/or up to about 30% by weight tin. Accordingly, in a preferred aspect this invention resides in a method of producing firescale resistant, work hardenable silver alloy compositions including the alloying of silver metal with a master alloy comprising, by weight:

15.0 - 99.545% by weight copper;

0.25 - 25% by weight zinc;

0.1 - 10% by weight silicon;

0.005 - 10% by weight boron;

0.05 - 15% by weight indium, and

0.05 - 25% by weight germanium.

In a yet further aspect this invention resides in a method of producing firescale resistant, work hardenable silver alloy compositions including the alloying of silver metal with a master alloy comprising, by weight:

2.5 - 97.455% by weight copper;

0.25 - 25% by weight zinc;

0.1 - 10% by weight silicon;

0.005 - 10% by weight boron;

0.05 - 15% by weight indium;

0.05 - 25% by weight germanium, and

2.0 - 12.5% by weight tin.

In a yet further aspect this invention resides in a method of producing firescale resistant, work hardenable silver

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alloy compositions including the alloying of silver metal with a master alloy comprising, by weight:

2.5 - 97.455% by weight copper;
0.25 - 19.85% by weight zinc;
0.1 - 7.94% by weight silicon;
0.005 - 7.94% by weight boron;
0.05 - 11.92% by weight indium;
0.05 - 19.85% by weight germanium, and
2.0 - 30% by weight tin.

In order that this invention may be more readily understood and put into practical effect, reference will now be made to the following example which describes a preferred embodiment of the invention.

EXAMPLE 1

An alloy consisting of the following constituents (by weight) and being in accordance with United States patent No. 5039479 was provided as a first control:

silver	92.5%
copper	3.29%
zinc	3.75%
indium	0.25%
boron	0.01%
silicon	0.2%

This alloy is known as and will be referred to hereinafter as "UPM alloy". As a second control, a commercial sterling silver was used, comprising 92.5 % by weight silver and the balance mainly copper.

Samples of the controls were cast and the hardness of each were measured as cast, at 50% and 75% work and annealed, according to the Vickers hardness VH scale. As used hereinafter the terms "50% work" and "75% work" mean subjecting a cast sample to cold rolling to 50% and 25% of its original thickness respectively.

Three alloys A to C in accordance with the present invention were prepared to the following compositions:

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	ALLOY A	ALLOY B	ALLOY C
Ag	92.5	92.5	92.5
Cu	2.35	3.25	3.0
Zn	2.82	3.75	3.14
Si	0.19	0.2	0.15
B	0.01	0.01	0.01
In	0.23	0.25	0.2
Ge	1.9	0.04	1.0

The three alloys were cast into samples as per the controls and were tested for Vickers Hardness as cast, at 50% and 75% work and annealed. The hardness results for the controls and alloys A, B, and C are as follows:

ALLOY	VH AS CAST	VH @ 50% WORK	VH @75% WORK	VH ANNEALED
STERLING	75.4	133	150	59
UPM	67	135	153	58.3
A	70.2	146	150	59.6
B	72.4	135	143	61.3
C	77.2	123	159	63.6

It can be seen that the alloy B having only 0.04% by weight Ge is harder than UPM and softer than sterling when cast, but that all three alloys are on par at 50% work. Alloy B exhibited a softening relative to the controls at 75% work and is hardest relative to the controls when annealed. Alloy C, having 1.0% by weight Ge, exhibits an as-cast hardness on par with sterling, is softer than UPM or sterling at 50% work, but is markedly harder than these two alloys at 75% work. Alloy A, having 1.9% by weight Ge, exhibits as-cast hardness between that of UPM and sterling, is markedly harder than these two alloys at 50% work, but does not increase hardness as much as the controls upon further work to 75%.

EXAMPLE 2

A firescale resistant, work hardening 925 silver alloy was prepared in accordance with the following formula, expressed as percentages by weight:-

Zinc	2.25
Indium	0.075
Tin	0.075
Germanium	0.125
Boron	0.003
Silicon	0.20
Copper	4.772
Silver	92.50

This alloy exhibited an as-cast Vickers hardness of approximately 15% greater than the firescale resistant alloy prepared without addition of germanium.

In use, alloys in accordance with the above embodiments and in accordance with the present invention may be selected by tailoring the germanium content of the alloys to provide

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the desired work hardening characteristics. The non-linear effect of use of germanium and the ability to vary other elements such as copper provides for production of a range of firescale resistant alloys of selected as-cast hardness and work hardenability.

It will of course be realised that while the above has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of this invention as defined in the claims appended hereto.

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CLAIMS:-

1. Firescale resistant, work hardenable jewellery silver alloy compositions comprising:-

0.5 - 6% by weight copper;

0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and

0.01 - 2.5% by weight germanium.

2. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 1, including silver in a content of at least 92.5% by weight.

3. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 1, including a copper content in the range of from 2.0 to 3.0% by weight.

4. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 1, including a zinc content between 2.0 and 4.0% by weight.

5. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 1, including a silicon content in the range of 0.15 to 0.2% by weight.

6. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 1, including a germanium content in the range of 0.04 to 2.0% by weight.

7. Firescale resistant, work hardenable jewellery silver alloy compositions comprising 0.0 to 3.5% by weight of a grain refinement and/or surface tension reducing additive selected from one or a mixture of indium and boron alloyed to a composition in accordance with any one of claims 1 to 6.

8. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 7, wherein said

grain refinement and/or surface tension reducing additive comprises from 0 to 2% by weight boron and 0 to 1.5% by weight indium.

9. Firescale resistant, work hardenable jewellery silver alloy compositions comprising tin in an amount of up to 6% by weight alloyed to a composition in accordance with any one of claims 1 to 6.

10. Firescale resistant, work hardenable jewellery silver alloy compositions in accordance with Claim 9, wherein the tin is utilized in an amount of from 0.25 to 6% by weight.

11. Silver alloy compositions comprising:-

81 - 99.409% by weight silver;
0.5 - 6% by weight copper;
0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
0.001 - 2% by weight boron;
0.01 - 1.5% by weight indium, and
0.01 - 2.5% by weight germanium.

12. Silver alloy compositions comprising:-

75 - 99.159% by weight silver;
0.5 - 6% by weight copper;
0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
0.001 - 2% by weight boron;
0.01 - 1.5% by weight indium;
0.01 - 2.5% by weight germanium, and
0.25 - 6.0% by weight tin.

13. A method of producing firescale resistant, work hardenable jewellery silver alloy compositions according to any one of Claims 1 to 10 and including the alloying of silver metal with a master alloy comprising, by weight:

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52.5 - 99.85% by weight copper;
0.1 - 35% by weight of zinc or silicon or mixtures thereof, and
0.05 - 12.5% by weight germanium.

14. A method of producing firescale resistant, work hardenable jewellery silver alloy compositions according to Claim 7 and including the alloying of silver metal with a master alloy comprising, by weight:

15.0 - 99.545% by weight copper;
0.25 - 25% by weight zinc;
0.1 - 10% by weight silicon;
0.005 - 10% by weight boron;
0.05 - 15% by weight indium, and
0.05 - 25% by weight germanium.

15. A method of producing firescale resistant, work hardenable jewellerysilver alloy compositions according to Claim 9 and including the alloying of silver metal with a master alloy comprising, by weight:

2.5 - 97.455% by weight copper;
0.25 - 25% by weight zinc;
0.1 - 10% by weight silicon;
0.005 - 10% by weight boron;
0.05 - 15% by weight indium;
0.05 - 25% by weight germanium, and
2.0 - 12.5% by weight tin.

16. A method of producing firescale resistant, work hardenable jewellery silver alloy compositions according to Claim 9 and including the alloying of silver metal with a master alloy comprising, by weight:

2.5 - 97.455% by weight copper;
0.25 - 19.85% by weight zinc;
0.1 - 7.94% by weight silicon;
0.005 - 7.94% by weight boron;

~~0.05 - 11.92% by weight indium;~~

~~0.05 - 19.85% by weight germanium, and~~

~~2.0 - 30% by weight tin.~~

17. A silver composition comprising, by weight percent:

Silver	92.5
Copper	2.35
Zinc	2.82
Silicon	0.19
Boron	0.01
Indium	0.23
Germanium	1.9

18. A silver composition comprising, by weight percent:

Silver	92.5
Copper	3.25
Zinc	3.75
Silicon	0.2
Boron	0.01
Indium	0.25
Germanium	0.04

19. A silver composition comprising, by weight percent:

Silver	92.5
Copper	3.0
Zinc	3.14
Silicon	0.15
Boron	0.01
Indium	0.2
Germanium	1.0

20. A silver composition comprising, by weight percent:

Zinc	2.25
Indium	0.075
Tin	0.075
Germanium	0.125

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Boron	0.003
Silicon	0.20
Copper	4.772
Silver	92.50

AMENDED SHEET

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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C22C 5/08, 5/06, 9/00, 9/04, 9/10, 30/06, 30/02, 1/03

A1

(11) International Publication Number: WO 95/14112

(43) International Publication Date: 26 May 1995 (26.05.95)

(21) International Application Number: PCT/AU94/00351

(22) International Filing Date: 27 June 1994 (27.06.94)

(30) Priority Data: PM 2432 15 November 1993 (15.11.93) AU

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

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(74) Agent: PIZZEY & COMPANY; Level 6, Trustee House, 444 Queen Street, Brisbane, QLD 4000 (AU).

Published
With international search report.

(54) Title: SILVER ALLOY COMPOSITIONS

(57) Abstract

Silver alloys having properties of fire scale resistance, reduced porosity and oxide formation and reduced grain size relative to traditional sterling silver alloys and useful work hardening performance are provided, comprising about 80 - 99.0 % by weight silver, about 0.5 - 6 % by weight copper, about 0.02 - 7 % by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and about 0.01 - 2.5 % by weight germanium. Master alloys for production of the above alloys are also provided for, having the general composition comprising, by weight, about 2.5 - 99.85 % copper, about 0.1 - 35 % zinc or silicon or mixtures thereof, and about 0.05 - 12.5 % germanium.

Rec'd PCT/PTO MAY 08 1996
08/637802

SILVER ALLOY COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to silver alloy compositions.

This invention has particular reference to sterling silver alloy compositions of silver content of at least 92.5% for jewellery, flatware, coinage and other applications where a work hardening alloy is required and for illustrative purposes reference will be made to this application. However, it is to be understood that this invention could be used to produce other types of silver alloys suitable for use as for example, electrical contacts or the like.

BACKGROUND OF THE INVENTION

In general, silver as a material for the production of silver jewellery, certain coinage and the like is specified to be sterling silver comprising at least 925 parts per thousand by weight fine silver and is specified as ".925 silver". .925 silver accordingly typically comprises an alloy 92.5% by weight silver, generally alloyed with copper for hardness traces of other metals as additives or impurities.

Conventional silver alloys of the .925 type have several disadvantages in a manufacturing jewellery and other materials engineering contexts. Principal limitations include a characteristic firescale formation tendency attributable to oxidation of copper and other metals at the surface of cast or hot worked pieces. Additionally, traditional alloys have exhibited undesirable porosity in the recast metal and less than desirable grain size properties.

Several formulations have been proposed to overcome one or the other of the aforementioned disadvantages. United States Patent Nos. 5039479 and 4973446 disclose alloys of silver and master alloys for the production of such silver alloys having superior qualities over conventional alloys, and including, in addition to silver, controlled amounts of copper and zinc, together with tin, indium, boron and silicon.

16NAB
Spec

The compositions exhibit reduced porosity, grain size and fire scale production, and have acquired wide utilization in silver jewellery production. It is presumed but not established that the addition of zinc to such compositions provides at least a degree of antioxidant properties to the compositions when hot worked and improves colour, thus limiting the formation of principally copper oxide based fire scale, and reducing silver and copper oxide formation resulting in formation of pores in the cast or recast alloys. Silicon appears also to function as an antioxidant, thereby reducing firescale formation.

A disadvantage of the hereinbefore described firescale resisting alloys is that the alloys exhibit poor work hardening qualities thus not achieving the mechanical strength of traditional worked .925 silver goods.

DISCLOSURE OF THE INVENTION

The present invention aims to provide silver alloy compositions which substantially alleviate at least one of the foregoing disadvantages. A further object of the present invention is to provide silver alloys having the desirable properties of reduced fire scale, reduced porosity and oxide formation and reduced grain size relative to traditional sterling silver alloys whilst providing improved work hardening performance over the current firescale resistant alloys. Other objects and advantages of this invention will hereinafter become apparent.

With the foregoing and other objects in view, this invention in one aspect resides broadly in silver alloy compositions including:-

about 80 - 99.0% by weight silver;

about 0.5 - 6% by weight copper;

about 0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and

about 0.01 - 2.5% by weight germanium.

The silver content of the alloy may be selected to be in

the amounts commonly specified for grading silver. For example, the alloy may comprise from about 89 to 95% by weight silver. Preferably, the alloy contains a proportion of silver required for the graded application to which the alloy is to be put, such as .925 silver, that is at least 92.5% by weight, for sterling silver applications and at least 90% by weight for coinage.

The copper content of the alloy may be selected according to the hardness required of the cast alloy. For example, for manufacturing jewellers .925 alloy, the copper content may advantageously be in the range of from about 2.0 to 3.0% by weight.

The zinc content of the alloy has a bearing on the colour of the alloy as well as functioning as a reducing agent for silver and copper oxides. Preferably, the amount of zinc used is selected to be between about 2.0 and 4.0% by weight. The silicon content of the alloy is preferably adjusted relative to the proportion of zinc used to provide the desired firescale resistance whilst maintaining a suitable colour commensurate with the zinc content of the alloy, and may for example advantageously fall within the range of about 0.15 to 0.2% by weight.

The germanium content of the alloy has surprisingly resulted in alloys having work hardening characteristics of a kind with those exhibited by conventional .925 silver alloys, together with the firescale resistance of the hereinbefore described firescale resistant alloys. In general, it has been determined that amounts of germanium in the alloy of from about 0.04 to 2.0% by weight provide modified work hardening properties relative to alloys of the firescale resistant kind not including germanium. However, it is noted that the hardening performance is not linear with increasing germanium nor is the hardening linear with degree of work.

Preferably, the alloy also includes rheology modifying and other additives to aid in improving the castability and/or wetting performance of the molten alloy. For example,

about 0.0 to 3.5% by weight of a modifying additive selected from one or a mixture of indium and boron may be advantageously added to the alloy to provide grain refinement and/or reduce surface tension, thereby providing greater wettability of the molten alloy. Where used, preferably the amount of boron utilized in the composition is from about 0 to 2% by weight boron and/or about 0 to 1.5% by weight indium. Other alloying elements may be added such as gold, tin or platinum. Where tin is included in the composition, this may be advantageously used up to about 6% by weight, and is preferably utilized in an amount of from about 0.25 to 6%.

Accordingly, in a further aspect, this invention resides in silver alloy compositions including:-

about 89 - 95% by weight silver;
about 0.5 - 6% by weight copper;
about 0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
about 0.001 - 2% by weight boron;
about 0.01 - 1.5% by weight indium, and
about 0.01 - 2.5% by weight germanium.

In a further aspect, this invention resides in silver alloy compositions including:-

about 89 - 95% by weight silver;
about 0.5 - 6% by weight copper;
about 0.05 - 5% by weight zinc;
about 0.02 - 2% by weight silicon;
about 0.001 - 2% by weight boron;
about 0.01 - 1.5% by weight indium;
about 0.01 - 2.5% by weight germanium, and
about 0.25 - 6.0% by weight tin.

Of course, it is of advantage to the manufacturing metallurgist to be able to alloy fine silver without having to individually measure components. Accordingly, it is preferred that the compositions of the present invention be formed by the addition of a master alloy to fine silver. This also has the advantage that the master alloys are easier

to transport than the made up alloys. Additionally, oxidizable components of the alloy are more stable to atmospheric oxidation when alloyed. Accordingly, in a further aspect this invention resides broadly in master alloy compositions for the production of silver alloys and including, by weight:

about 2.5 - 99.85% by weight copper;

about 0.1 - 35% by weight of zinc or silicon or mixtures thereof, and

about 0.05 - 12.5% by weight germanium.

For production of the preferred modified alloys, there may be provided master alloys including additional alloying elements such as up to about 10% by weight boron, up to about 15% by weight indium and/or up to about 30% by weight tin. Accordingly, in a preferred aspect this invention resides in master alloys for the production of silver alloys and including:

15 99.545

14.99 about 2.5 - 99.55% by weight copper;

about 0.25 - 25% by weight zinc;

about 0.1 - 10% by weight silicon;

about 0.005 - 10% by weight boron;

about 0.05 - 15% by weight indium, and

about 0.05 - 25% by weight germanium.

In a yet further aspect this invention resides in master alloys for the production of silver alloys and including:

15.9 about 2.5 - 99.55% by weight copper; 454 -97.455

about 0.25 - 25% by weight zinc; -19.85

about 0.1 - 10% by weight silicon; 7.94

about 0.005 - 10% by weight boron; .05 .005-7.94

about 0.05 - 15% by weight indium; -11.92

about 0.05 - 25% by weight germanium, and -19.85

about 2.0 - 30% by weight tin. 12.5 2-30

In order that this invention may be more readily understood and put into practical effect, reference will now be made to the following example which describes a preferred embodiment of the invention.

EXAMPLE 1

An alloy consisting of the following constituents (by weight) and being in accordance with United States patent No. 5039479 was provided as a first control:

silver	92.5%
copper	3.29%
zinc	3.75%
indium	0.25%
boron	0.01%
silicon	0.2%

This alloy is known as and will be referred to hereinafter as "UPM alloy". As a second control, a commercial sterling silver was used, comprising 92.5 % by weight silver and the balance mainly copper.

Samples of the controls were cast and the hardness of each were measured as cast, at 50% and 75% work and annealed, according to the Vickers hardness VH scale. As used hereinafter the terms "50% work" and "75% work" mean subjecting a cast sample to cold rolling to 50% and 25% of its original thickness respectively.

Three alloys A to C in accordance with the present invention were prepared to the following compositions:

	ALLOY A	ALLOY B	ALLOY C
Ag	92.5	92.5	92.5
Cu	2.35	3.25	3.0
Zn	2.82	3.75	3.14
Si	0.19	0.2	0.15
B	0.01	0.01	0.01
In	0.23	0.25	0.2
Ge	1.9	0.04	1.0

The three alloys were cast into samples as per the controls and were tested for Vickers Hardness as cast, at 50% and 75% work and annealed. The hardness results for the controls and alloys A, B, and C are as follows:

ALLOY	VH AS CAST	VH @ 50% WORK	VH @75% WORK	VH ANNEALED
STERLING	75.4	133	150	59
UPM	67	135	153	58.3
A	70.2	146	150	59.6
B	72.4	135	143	61.3
C	77.2	123	159	63.6

It can be seen that the alloy B having only 0.04% by weight Ge is harder than UPM and softer than sterling when cast, but that all three alloys are on par at 50% work. Alloy B exhibited a softening relative to the controls at 75% work and is hardest relative to the controls when annealed. Alloy C, having 1.0% by weight Ge, exhibits an as-cast hardness on par with sterling, is softer than UPM or sterling at 50% work, but is markedly harder than these two alloys at 75% work. Alloy A, having 1.9% by weight Ge, exhibits as-cast hardness between that of UPM and sterling, is markedly harder than these two alloys at 50% work, but does not increase hardness as much as the controls upon further work to 75%.

EXAMPLE 2

A firescale resistant, work hardening 925 silver alloy was prepared in accordance with the following formula, expressed as percentages by weight:-

Zinc	2.25
Indium	0.075
Tin	0.075
Germanium	0.125
Boron	0.003
Silicon	0.20
Copper	4.772
Silver	92.50

This alloy exhibited an as-cast Vickers hardness of approximately 15% greater than the firescale resistant alloy prepared without addition of germanium.

In use, alloys in accordance with the above embodiments and in accordance with the present invention may be selected by tailoring the germanium content of the alloys to provide

the desired work hardening characteristics. The non-linear effect of use of germanium and the ability to vary other elements such as copper provides for production of a range of firescale resistant alloys of selected as-cast hardness and work hardenability.

It will of course be realised that while the above has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of this invention as defined in the claims appended hereto.

CLAIMS

1. Silver alloy compositions including:-

about 80 - 99.0% by weight silver;

about 0.5 - 6% by weight copper;

about 0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and

about 0.01 - 2.5% by weight germanium.

2. Silver alloy compositions in accordance with Claim 1, wherein the silver content of the alloy is at least 92.5% by weight.

3. Silver alloy compositions in accordance with Claim 1, wherein the copper content of the alloy is in the range of from about 2.0 to 3.0% by weight.

4. Silver alloy compositions in accordance with Claim 1, wherein the zinc content of the alloy is selected to be between about 2.0 and 4.0% by weight.

5. Silver alloy compositions in accordance with Claim 1, wherein the silicon content of the alloy is in the range of about 0.15 to 0.2% by weight.

6. Silver alloy compositions in accordance with Claim 1, wherein the germanium content of the alloy is in the range of about 0.04 to 2.0% by weight.

7. Silver alloy compositions in accordance with Claim 1, wherein the alloy includes about 0.0 to 3.5% by weight of an additive selected from one or a mixture of indium and boron. and/or

8. Silver alloy compositions in accordance with Claim 7, wherein the additive utilized in the composition is from about 0 to 2% by weight boron and about 0 to 1.5% by weight and/or

indium.

9. Silver alloy compositions in accordance with Claim 1, wherein tin is included in the composition in an amount of up to about 6% by weight.

10. Silver alloy compositions in accordance with Claim 9, wherein the tin is utilized in an amount of from about 0.25 to 6%.

11. Silver alloy compositions including:-

81 99.409

about 89 - 95% by weight silver;
about 0.5 - 6% by weight copper;
about 0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
about 0.001 - 2% by weight boron;
about 0.01 - 1.5% by weight indium, and
about 0.01 - 2.5% by weight germanium.

12. Silver alloy compositions including:-

75 99.159

about 89 - 95% by weight silver;
about 0.5 - 6% by weight copper;
about 0.05 - 5% by weight zinc;
about 0.02 - 2% by weight silicon;
about 0.001 - 2% by weight boron;
about 0.01 - 1.5% by weight indium;
about 0.01 - 2.5% by weight germanium, and
about 0.25 - 6.0% by weight tin.

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13. Master alloy compositions for the production of silver alloys and including, by weight: make 9

97.455

about 2.5 - 99.85% by weight copper;
about 0.1 - 35% by weight of zinc or silicon or mixtures thereof, and
about 0.05 - 12.5% by weight germanium.

14. Master alloys for the production of silver alloys and including:

about 2.5 - 99.55% by weight copper;
about 0.25 - 25% by weight zinc;
about 0.1 - 10% by weight silicon;
about 0.005 - 10% by weight boron;
about 0.05 - 15% by weight indium, and
about 0.05 - 25% by weight germanium.

15. Master alloys for the production of silver alloys and including:

about 2.5 - 99.55% by weight copper;
about 0.25 - 25% by weight zinc;
about 0.1 - 10% by weight silicon;
about 0.005 - 10% by weight boron;
about 0.05 - 15% by weight indium;
about 0.05 - 25% by weight germanium, and
about 2.0 - 30% by weight tin.

16. A silver composition including, by weight percent:

Silver	about 92.5
Copper	about 2.35
Zinc	about 2.82
Silicon	about 0.19
Boron	about 0.01
Indium	about 0.23
Germanium	about 1.9

17. A silver composition including, by weight percent:

Silver	about 92.5
Copper	about 3.25
Zinc	about 3.75
Silicon	about 0.2
Boron	about 0.01
Indium	about 0.25
Germanium	about 0.04

18. A silver composition including, by weight percent:

Silver	about 92.5
Copper	about 3.0
Zinc	about 3.14
Silicon	about 0.15
Boron	about 0.01
Indium	about 0.2
Germanium	about 1.0

19. A silver composition including, by weight percent:

Zinc	about 2.25
Indium	about 0.075
Tin	about 0.075
Germanium	about 0.125
Boron	about 0.003
Silicon	about 0.20
Copper	about 4.772
Silver	about 92.50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 94/00351

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[6] C22C 5/08, 5/06, 9/00, 9/04, 9/10, 30/06, 30/02, 1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : as above

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	Derwent Abstract Accession No. 24286Y/14, Class L03, JP 52-023660 (TANAKA KIKINZOKU KK) 22 February 1977 (22.02.77) Abstract	1-4,6-10,13
X	Derwent Abstract Accession No. 93-012634/02, Class P23, JP 04-339500 (CITIZEN WATCH CO LTD) 26 November 1992 (26.11.92) Abstract	1,4,6-10,13
X	Derwent Abstract Accession No. 86-086006/13, Class V04, JP 61-034144 (TANAKA KIKINZOKU KK) 18 February 1986 (18.02.86) Abstract	1-3,6,13

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 September 1994 (08.09.94)	15 Sept 1994 (15.09.94)

Name and mailing address of the ISA/AU	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	Patent Abstracts of Japan, M-192, page 156, JP 57-187195 (TOKURIKI HONTEN KK) 17 November 1982 (17.11.82) Abstract	1,2,5,6,13
X	Patent Abstracts of Japan, C-83, page 148, JP 56-119747 (NIPPON DENSHIN DENWA KOSHA) 19 September 1981 (19.09.81) Abstract	1-3,6,13
X	Patent Abstracts of Japan, C-357, page 94, JP 61-34147 (TANAKA KIKINZOKU (KOGYO KK) 18 February 1986 (18.02.86) Abstract	1,2,6,13
X	Derwent Abstract Accession No. 92-320122/89, Class V04, JP 04-224645 (NIPPON MINING CO) 13 Aaugust 1992 (13.08.92) Abstract	13-15
X	Derwent Abstract Accession No. 91-152508/21, Class M26, JP 03-087325 (NIPPON MINING KK) 12 April 1991 (12.04.91) Abstract	13,14
X	Derwent Abstract Accession No. 91-262404/36, Class M26, JP 03-170646 (NIPPON MINING KK) 24 July 1991 (24.07.91) Abstract	13,14
X	Derwent Abstract Accession No. 85-149928/25, Class M26, JP 60-082635 (NIPPON MINING KK) 10 May 1985 (10.05.85) Abstract	13,14
X	EP,A1, 64181 (SIEMENS AG) 10 November 1981 (10.11.81) See claims 1-2	13

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	64181	AT	11840	DE	3116680	ES	511703
		FI	820583	GR	75432	JP	57181348
		NO	821339	PT	74797	ZA	8202858
							END OF ANNEX